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<b>(54) Title:</b> METHOD FOR MAKING PREFORMS  <b>(57) Abstract</b>  Partially or wholly melted binder particles are sprayed onto a fiber mat to form a preform. A fast, low energy method for making preforms is thus provided.		

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## METHOD FOR MAKING PREFORMS

This invention relates to a method of making a preform suitable for use in making reinforced thermoplastic or thermoset composites.

5           There is an increasing need for high strength polymeric materials to replace metals in many applications. The polymeric materials have the advantage of lower weight and are often less expensive and more durable than metals. Usually, however, the polymeric material is much lower in strength than the metal, and unless it is reinforced in some manner it will not meet the strength requirements for metal replacement.

10           Thus, polymeric composites have been developed to meet these strength requirements. These composites are characterized by having a continuous polymeric matrix in which is embedded a reinforcement, usually a relatively rigid, high aspect ratio material such as glass fibers.

          These composites usually are molded into a predetermined shape. In order to get  
15 the reinforcement into the composite, it is usually placed into the mold in a first step, followed by closing the mold and introducing a fluid molding resin into the mold. The molding resin fills the mold, including the interstices between the fibers, and hardens (by cooling or curing) to form the desired composite.

          The reinforcement must be uniformly distributed throughout the composite or  
20 the composite will have weak spots where the reinforcement is missing. Thus, the reinforcement must be prepared so the individual fibers are distributed evenly throughout the composite. In addition, the individual fibers must resist flowing with the molding resin as it enters the mold.

          For these reasons, the reinforcement is typically formed into a mat outside of the  
25 mold, and the preformed mat is placed in the mold in order to make the composite. The mat is generally prepared by forming the reinforcing fibers into a shape matching the inside of the mold and applying a binder to the fibers. In some instances a thermosetting binder is preapplied, and then cured after the fibers are shaped into a mat. In other methods, a thermoplastic binder is applied, so that in a subsequent operation the binder can be heated

and softened and the mat shaped. This binder "glues" the individual fibers to each other so that the resulting mat retains its shape when it is transferred to the mold. The binder also helps the individual fibers retain their position when the fluid molding resin is introduced into the mold.

5               The binders used heretofore have been primarily of two types. The predominately used binders have been solvent-borne polymers such as epoxy resins. In addition, powdered binders have also been used. The conventional use of each of these types of binders has significant drawbacks. The solvent-borne binders are usually sprayed onto the mat, and then the mat is heated to volatilize the solvent and if necessary cure the binder. Thus, 10 the application of binder is at least a two-step process. Moreover, it involves the use of solvents, which raises environmental, exposure and recovery issues, adding to the expense of the process. The process is also energy intensive, as the entire mat must be heated just to flash off solvent and cure the binder. The curing step also makes the process take longer. In the preferred air directed method using this type of binder, "lofting", or inadequate compaction 15 of the preform, occurs. This causes the formation of a lower density preform than desired, density gradients throughout the preform, and poor adhesion of the individual fibers to the others. Finally, because the binder is a low viscosity fluid, it tends to flow over and coat a large portion of the surface of the fibers. When a composite is prepared using the preform, the binder often interferes with the adhesion between the fiber and the continuous polymer 20 phase.

              The powdered binders cannot be applied to a screen in an air directed method, unless a veil is first applied to the screen to prevent the binder particles from being sucked through. This of course adds to the overall cost and imposes an additional step on the process. Airborne powders also present a health and explosion hazard. Further, the use of powdered 25 binders requires a heating step to melt the binder particles after they are applied to the fibers, which renders this process energy intensive as well.

              Thus, it would be desirable to provide a simpler method for making preforms in which the problems associated with using solvent-borne or powdered binders are minimized or overcome.

30               In one aspect, this invention is a method for applying a binder to a fiber mat, comprising

              (a) applying a plurality of particles of an at least partially melted tacky binder material onto a fiber mat, which material is solid at 25°C, said particle being used in an amount from 0.25 to 20 parts per 100 parts by weight fiber mat and then

35               (b) cooling said binder material to a temperature at which it is solid such that the particles adhere to the fibers in the mat and bind said fibers together to form a dimensionally stable preform.

In another aspect, this invention is a method for applying a binder to a fiber mat, comprising

- (a) spraying a plurality of particles of a material which is a solid at 25°C through an energy source such that the particles are at least partially melted so as to become tacky,
- (b) contacting said at least partially melted particles with a fiber mat said particle being used in an amount from 0.25 to 20 parts per 100 parts by weight fiber mat and then
- (c) cooling said particles to a temperature at which they are solid such that the particles adhere to the fibers in the mat and bind said fibers together to form a dimensionally stable preform.

In a third aspect, this invention is a method for making a preform, comprising

- (a) applying a plurality of short reinforcing fibers to a screen to form a shaped mat
- (b) spraying a plurality of particles of an at least partially tacky binder material such that said particles come into contact with said mat, which material is a solid at 25°C, then, while maintaining said fibers in position on the screen,
- (c) cooling said binder material to a temperature at which it is solid, whereby the binder material adheres to the fibers in the mat and binds said fibers together to make a dimensionally stable preform, and then
- (d) removing the resulting preform from the screen.

This method provides for a simplified, effective method for making preforms. Because the binder material is a true solid or supercooled liquid at 25°C, volatile organics such as solvents are not present in significant amounts, and the problems associated with them are avoided. The preform does not have to be heated after application of the binder to remove solvent or cure the binder, and so a process step is saved and energy requirements are reduced. Since the binder is applied in a finely divided state, the cooling step is usually almost instantaneous, so the process is fast. In addition, the fibers in the mat are often compacted during this process, thereby providing a higher density preform, which in turn provides a way to obtain higher fiber loadings in a composite material made from the preform. Since the binder cools rapidly it immediately holds the fibers in place and thus overcomes the lofting problem associated with solvent-borne and powdered binders. For this same reason, the binder particles do not spread much from their point of impact on the fibers. Thus, the surface area of the fibers which is covered with binder is substantially reduced compared to when the solvent-borne binders are used. This maximizes the available surface area of the fibers available for direct interface with the molding resin when a composite is made, and therefore enables a greater interfacial bond strength to be obtained.

In this process, a normally solid binder material is applied to a mat of reinforcing fibers as a plurality of at least partially melted, tacky particles. The particles then cool in contact with the fibers of the mat, gluing them together to make a preform. As used herein, the term "mat" refers to a collection of intersecting fibers to which no binder is applied. The term "preform" refers to a collection of intersecting fibers to which a binder has been applied. The preform may or may not be shaped to a particular configuration for making a particular molded composite.

The binder material is a solid at 25°C. The term "solid" is used herein to include true solids as well as supercooled materials such as glass. Similarly, the terms "melt" or "molten" are used broadly herein to describe true melting as well as the heating of a supercooled liquid to a fluid state. The binder must be capable of melting so that it can be applied to the mat without significant decomposition. Further, it must be such that it adheres to the fibers of the mat upon cooling, forming a preform capable of maintaining its shape upon further handling. It is also preferably of a composition such that it does not significantly degrade under the temperature conditions encountered during preform preparation or subsequent molding operations.

Accordingly, the binder can be of a wide variety of compositions. Noncellular or cellular polymers which melt or soften without substantial decomposition are useful. Ceramic materials such as glass can also be used, as well as metals, especially low-melting metals. The selection of the composition of the binder may depend somewhat on whether any special properties are desired in the preform, as described below.

It is generally preferred to use an organic polymer as the binder material. A wide variety of organic polymers can be used, provided they meet the requirements set out before. Those having a melting point or  $T_g$  from 40, preferably 45 to 220, preferably to 180, more preferably to 150°C are of particular interest. Thermoplastic polymers are preferred, since those polymers melt easily without significant decomposition and solidify to adhere to the binder. However, thermoset polymers which can soften to become tacky upon heating can also be used herein. Among the thermoplastic resins useful herein are vinyl polymers and copolymers, including homopolymers and interpolymers of ethylene, propylene, and styrene, conjugated dienes such as butadiene, acrylics such as alkyl acrylates, acrylamide, acrylonitrile, alkyl methacrylates, hydroxy-alkylacrylates or methacrylates, vinyl halides like vinylchloride, vinylidene halides such as vinylidene chloride. Other types of thermoplastic polymers, including polyamines, polyesters, polycarbonates, thermoplastic polyurethanes and linear epoxy resins are also useful. A preferred organic polymer is an epoxy resin, particularly a substantially linear solid epoxy resin, especially a diglycidyl ether of a bisphenol. Suitable such epoxy resins include those described in

U. S. Patent No. 4,992,228. Normally the polymeric binders are non-cellular, but cellular polymers as well as expandable polymers can also be used. In order to optimize adhesion of the

molding resin to the preform when the composite is prepared, it is desirable to use a binder material which is compatible with the molding resin.

In addition to the preferred organic polymer binders, materials such as glass and other ceramic materials, metals (particularly low melting metals and alloys) and waxes can be used as the binder. Metal binders are of particular interest when it is desired to prepare a conductive preform. The ceramics and metals preferably have a melting point (or  $T_g$ , as the case may be) of less than about 700°C, preferably 100 to 500°C. This melting point range is preferred as, at those temperatures, the particles are melted easily and quickly cool to resume a solid state.

The binder normally and preferably contains no more than a small amount of volatile organic materials, so as not to require a drying step after application, and to avoid the environmental and health risks associated with the presence of volatile organics. A volatile organics content of 5 percent or less by weight, preferably 2 percent or less by weight is thus desired. In particular, it is preferred that any organic polymer used as a binder be substantially free of solvent and most preferred that an essentially 100 percent solids organic polymer be used.

The binder is in the form of a particulate. The term particulate is used herein to refer not only to generally solid low aspect ratio (about 3 or less) particles, but also to short fibers, hollow structures such as glass microbubbles or polymer foam particles. The size of the particles is not especially critical, although their particle size as well as their particular composition do effect melting rate, which in turn affects the amount of heating needed. For low aspect ratio materials, particles of 10 to 250 mesh (U. S. Standard) are generally useful, with those of 50 to 100 mesh particularly useful. For high aspect ratio (greater than 3) binders, diameters of from 1, preferably from 10 to 500 microns, preferably at about 100 microns, more preferably to 30 microns are generally of interest.

In this process, the binder material is melted and sprayed onto a fiber mat, on which it cools and adheres the individual fibers of the mat together.

The mat is composed of a fibrous reinforcing material. For the purposes of this invention, a fiber is a material having an aspect ratio of at least about 5, preferably at least about 10 and a length of at least about 0.1 inch, preferably at least about 0.25 inch. The fiber can be continuous, but preferably consists of chopped fibers having an average length of up to about 18 inches, preferably up to about 10 inches, more preferably up to about 4 inches. Fiber diameters in the range from 1 to 1000 microns are generally useful. The fiber may be monofilament, multistrand, woven or non-woven. Fiber rovings are also useful. The fibers can be of varying composition, provided that they do not melt as a composite is made therewith, and in general are chosen so that the fibers are stiffer (have a higher flexural modulus) than the molding resin used in the composite. Thus, high flexural modulus organic polymers such as polyamides, polyimides and aramids, metals, glass and other ceramics, carbon fibers and

graphite fibers are suitable fiber materials. Glass fibers, including E glass and S glass, are preferred in many instances because of cost, availability and excellent reinforcing properties.

The fibers are formed into a mat using any convenient method. For example, continuous fibers can be woven to form a mat. In this method, the mat can be shaped for  
5 insertion into a mold prior to applying the binder. Alternatively, the binder can be applied to the woven mat, and the resulting preform heated and shaped in subsequent operations. In the latter case, a thermoplastic binder is especially useful.

In a similar manner, a mat can be made by forming a continuous fiber into loops. This type of mat can be shaped for insertion into a mold before or after applying the binder. As  
10 with the woven mats, it is highly preferred to use a thermoplastic binder for this type of mat, for the same reasons.

A third method is an air directed method in which chopped fibers are blown onto a shaped screen. The screen is normally shaped to match the contours of the mold. Air is drawn through the screen to hold the fibers in place until the binder is applied and cooled. This  
15 process is described more fully by Carley et al., "Preforming for Liquid Composite Molding," 44th Annual Conference, Composites Institute, The Society of the Plastics Industry, Inc., February 6-9, 1989.

The dimensions of the mat are not particularly critical as long as sufficient binder can be applied to the mat to give the resulting preform enough mechanical integrity to be  
20 transferred to a mold and used to make a composite. Mat thickness of up to 1 inch, preferably up to 0.5 inch, more preferably 0.125 to 0.4 inch, are typically suitable. Of course, the mat thickness will depend on the particular part to be made therewith. Mat weights of 0.1 to 10 kg/m<sup>2</sup> can be prepared in this method, with weights from 0.5 to 6 kg/m<sup>2</sup> being typical. It is an advantage of this invention that higher density preforms (4 to 10 kg/m<sup>2</sup>) can be prepared  
25 easily.

The binder is applied as a plurality of at least partially melted tacky particles. Methods for applying the particles fall into two general classes. The preferred method involves forming a particulate solid binder material, and then spraying the binder particles through a heat source, and then onto the mat. The heat source is such that the binder material is at least  
30 partially melted, as discussed before. The preferred heat source is a flame, but other heat sources such as microwave or infrared radiation or a convection oven may also be useful. Most preferably, a flame spray apparatus such as that sold under the trade name Uni-Spray-Jet by UTP Welding Materials, Inc. is used to propel solid particles through a flame source and then onto the mat.

In another method, a bulk binder material is exposed to a heat source such as a  
35 flame, so that a portion thereof melts. A gas stream is then blown across the molten binder, causing particles of the molten material to be borne from the heat source onto the mat. This process is particularly useful for higher melting binder materials, such as glass or metals,



although it can be used with polymeric binders as well. This process has the advantage of using a binder in bulk form, thus eliminating the need for a particulate starting material.

Sufficient binder is applied so that the fibers of the mat are glued together enough that the resulting preform maintains its physical integrity upon subsequent handling and molding operations. In general, from 0.25, preferably from 1.0, more preferably from 2.0 to 20, preferably to 10 parts by weight binder are used per 100 parts by weight mat.

In the air directed method, the steps of mat formation and binder application may be done sequentially. However, it is possible to perform these steps simultaneously in an air directed method. Thus, the fibers and binder can be simultaneously applied to a screen to form a preform in a single step. This is particularly useful in preparing thicker preforms, as it enables the binder to be more evenly distributed through the fibers in the mat. Thicker preforms can also be prepared in an air directed method by applications of thin layers of fiber alternated with applications of binder. Thus, the steps of applying the fibers to a screen, and then applying the binder material can be carried out at least twice, each time increasing the thickness of the preform.

The mat formation and binder application steps are also normally done sequentially when woven or looped mats are used.

Once the binder particles are applied to the mat, they are cooled to a temperature at which they become solid (i.e. are cooled to a temperature below their melting point or  $T_g$ ). Usually, the mat acts as a heat sink, quickly removing heat from the binder particles. Thus, it is preferred that the mat be at a temperature below the melting point (or  $T_g$ ) of the binder metal. In the air directed method, the air flow through the mat also contributes to cooling. As mentioned before, this cooling often occurs almost instantaneously, so that the preform is ready for subsequent handling and use almost immediately. If necessary, additional cooling can be implemented, but it is normally unnecessary and thus preferably avoided.

This process has the potential advantage of permitting the use of a much wider variety of binders than previous processes. It works quite well with non-cellular polymeric binders, thus providing a faster and more economical method of making a preform. In addition, this process permits the use of materials which previously were not considered for use as binders. Glass and metals, for example can be used, thereby eliminating any organic polymer from the preform. The use of metals permits the preparation of conductive preforms. Foamed polymer particles or expandable thermoplastic beads can also be used as the binder. This permits the preparation of a preform bound with a low density material, which preform can then be used to make a composite having a reduced internal density, as is desired in forming lightweight structural parts.

Another advantage this process provides, when the air directed method is used, is that it permits one to prepare a large preform in several smaller sections. In conventional air directed methods, a high powered fan or blower was needed, since the fibers and binder had

to be applied to the entire screen, and the entire arrangement had to be maintained in place through the heating step, until the binder was cured. Because in this invention the binder immediately glues the individual fibers in place, the fibers can be applied to a small section of the screen, and will remain in place while fibers and binder are applied to subsequent sections.

- 5 In this manner, very small blowers or fans are needed, and thus the capital requirements and energy consumption of the air directed method are improved.

As another alternative, a non-melting filler material may be sprayed onto the mat before or simultaneously with the binder material. It may also be applied in an intermediate step such that the resulting preform has a "core" rich in such non-melting filler material  
10 sandwiched between outer binder layers. Such fillers include thermosetting polymers, inorganic fillers such as titanium dioxide, kaolin, wollastonite, mica, calcium carbonate and aluminum trihydrate. The organic polymer filler can be of several types, but recycled polyurethane scrap is of particular interest. By applying a filler in this manner, the filler can be applied evenly to the mat and bound to the mat by the binder material, thus reducing or  
15 eliminating altogether the problem of the filler particles falling out of the preform during handling, or being washed out when the resin is injected during composite formation.

Other modifications to the preform can be made as needed. For example, spot reinforcement, such as, for example, with a woven or non-woven support material, can be incorporated into the preform prior to or after the application of the binder, in order to  
20 provide areas of extra reinforcement. Directionally oriented reinforcing fibers can also be used for additional strength and reinforcement.

The resulting preform is useful in preparing composites. These processes generally involve shaping the preform to match the contours of a mold (if such is not already done as the preform is made), placing the shaped preform into a mold, injecting an uncured or  
25 melted molding resin into the mold, and then curing or cooling the molding resin as needed to form a solid molded polymer. Of particular interest are the so-called resin transfer molding (RTM) and structural reaction injection molding (SRIM) processes. Such processes are described, for example, by Vaccarella, "RTM: A Proven Molding Process", Section 24-A, Proceedings of the 38th Annual Conference, Society of the Plastics Industry, 1985, p. 1-8, and in U. S. Patent  
30 Nos. 4,810,444 and 4,863,994. Although thermoplastic polymers can be used for this purpose, they usually have melt viscosities that are too high for easy processing. The high viscosity of the thermoplastic polymers often causes them to flow very poorly around the fibers in the preform, causing the formation of void spaces or in some instances destruction of the preform. In addition, some thermoplastics which chemically debond at high temperatures should also be  
35 avoided. Thus, it is preferred to use an uncured thermoset resin, which can be injected as low viscosity liquid into the mold and then cured. Suitable thermosetting resins include epoxy resins, polyurethanes, vinyl ester resins, unsaturated polyesters and phenolic resins. Most preferred are the epoxy resins, vinyl ester resins, unsaturated polyesters and polyurethanes.

The most suitable epoxy resins are liquid at room temperature and are cured with a liquid reactant such as a polyamine. Particularly suitable epoxy resins include polyglycidyl ethers of polyhydric phenols such as, for example, diglycidyl ethers of biphenol, bisphenols, hydrocarbyl substituted biphenol and bisphenols, phenol or hydrocarbyl substituted bisphenol-aldehyde novolac resins, unsaturated hydrocarbon-phenol or hydrocarbyl substituted phenol resins and combinations thereof. Most particularly suitable are glycidyl ethers of bisphenol A having an epoxide equivalent weight from 350 to 2000, more preferably 600 to 1000.

Suitable vinyl ester and polyesters include those described in U. S. Patent No. 4,992,228. Suitable vinyl ester resins include, for example, the acrylate or methacrylates of polyglycidyl ethers of compounds having an average of more than one phenolic hydroxyl group per molecule. Most particularly suitable are the 500 to 2000 molecular weight reaction products of the glycidyl ether of bisphenol A and acrylic or methacrylic acid. Particular suitable unsaturated polyester resins include, for example, the reaction products of an unsaturated diacid such as fumaric acid with an alkoxyated bisphenol, such as a propoxylated or ethoxylated bisphenol A.

Suitable polyurethane resins include those described in U. S. Patent No. 4,810,444 and 4,863,994. Preferred polyurethanes are reaction products of a polyisocyanate and an active hydrogen-containing composition. The preferred polyisocyanates are toluene diisocyanate, diphenylmethanediisocyanate and derivatives of MDI such as polymeric MDI and prepolymers made from MDI. The active hydrogen-containing composition generally comprises one or more compounds having an average of two or more isocyanate-reactive groups per molecule and equivalent weights in the range from 31 to 3000. Preferably, a monofunctional material is also included in the active hydrogen-containing composition, as described in U. S. Patent No. 4,863,994. The active hydrogen-containing composition may further contain additives such as catalysts, colorants, surfactants and blowing agents.

The resulting composite is useful for a wide variety of uses, such as automobile bumpers, spare tire covers, computer housings, and in other structural applications.

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

#### Example 1

A glass fiber roving sold by Certainteed Corporation as Certainteed 227 roving was dispensed onto a 457 mm<sup>2</sup> screen having 3.2 mm diameter holes located on a 4.8 mm triangular pitch. The fibers were chopped into 32 mm lengths and blown onto the screen using a commercial chopper gun. A blower located on the reverse side of the screen pulls air through the screen to hold the fibers in place.

To the glass fibers was applied a molten thermoplastic epoxy resin. This resin was a diglycidyl ether of bisphenol A having a melting point of 55°C to 60°C and an epoxide equivalent weight of 675 to 750. The resin was applied by first grinding it to a mesh size of 50 to 100 (U. S. Standard). The resulting particulate was placed into the reservoir of a UTP  
5 Uni-Spray-Jet 71000 flame spray gun and sprayed through a propane/oxygen flame onto the fibers. The fibers of the preform were compressed by the force of the binder spray. The binder resolidified immediately upon contact with the fiber mat. The resulting preform had a density of 3.3 kg/m<sup>2</sup> and contained 9.6 percent binder (as measured by a glass burnout test). The thickness was 7 mm.

10 In a second experiment, a 9 mm thick preform weighing 5.1 kg/m<sup>2</sup> and containing 8.2 percent by weight binder was prepared in a similar manner. This preform was much more compact than conventional air directed fiber preforms, which were limited to a maximum density of about 3.6 kg/m<sup>2</sup>.

#### Example 2

15 A continuous glass roving (Rovcloth 3654, sold by Fiber glass Industries) was placed on a horizontal surface in the form of a woven mat. About 3 percent by weight of a binder was applied in the same manner as in Example 1. The resulting preform was stiff, and can be easily formed into any desired shape for molding by heating to about 100°C.

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## Claims:

1. A method for applying a binder to a fiber mat, comprising
  - (a) applying a plurality of particles of an at least partially melted tacky binder material onto a fiber mat, which material is solid at 25°C, said particle being used in an amount from 0.25 to 20 parts per 100 parts by weight fiber mat and then
  - 5 (b) cooling said binder material to a temperature at which it is solid such that the particles adhere to the fibers in the mat and bind said fibers together.
2. The method of Claim 1 wherein said binder material is a thermoplastic organic polymer and said fiber mat is composed of glass, graphite, carbon, or high flexural modulus organic polymer fibers.
- 10 3. The method of Claim 2 wherein said fibers have a diameter from 1 to 1000 microns, and 1 to 20 parts by weight binder are used per 100 parts by weight mat.
4. The method of Claim 3 wherein said binder material is an epoxy resin, and the fiber is glass having an average length of 0.25 to 10 inches.
5. The method of Claim 3 wherein the mat is composed of woven or looped
- 15 glass fibers.
6. A method for applying a binder to a fiber mat, comprising
  - (a) spraying a plurality of particles of a solid binder material which is solid at 25°C through an energy source such that the particles are at least partially melted so as to become tacky
  - 20 (b) contacting said at least partially melted particles with a fiber mat said particle being used in an amount from 0.25 to 20 parts per 100 parts by weight fiber mat and then
  - (c) cooling said particles to a temperature at which they are solid such that the particles adhere to the fibers in the mat and bind said fibers together.
- 25 7. The method of Claim 6 wherein said binder material is a thermoplastic organic polymer and said fiber mat is composed of glass, graphite, carbon, or high flexural modulus organic polymer fibers.
8. The method of Claim 7 wherein said fibers have a diameter from 1 to 1000 microns, and 1 to 20 parts by weight binder are used per 100 parts by weight mat.

9. The method of Claim 8 wherein said binder material is an epoxy resin, and the fiber is glass having an average length of 0.25 to 10 inches.
10. The method of Claim 8 wherein the mat is composed of woven or looped glass fibers.
- 5 11. A method for making a preform, comprising
- (a) applying a plurality of short reinforcing fibers to a screen to form a shaped mat
- (b) spraying a plurality of particles of an at least partially tacky binder material such that said particles come into contact with said mat, which material is a solid at 25°C, then, while maintaining said fibers in position on the screen,
- 10 (c) cooling said binder material to a temperature at which it is solid, whereby the binder material adheres to the fibers in the mat and binds said fibers together to make a dimensionally stable preform, and then
- (d) removing the resulting preform from the screen.
12. The method of Claim 11 wherein said fibers have a diameter from 1 to 1000
- 15 microns and an average length of 0.25 to 4 inches, and 1 to 20 parts by weight binder are used per 100 parts by weight mat.
13. The method of Claim 12 wherein said fibers are glass, graphite, carbon or a high flexural modulus organic polymer, and said binder material is a thermoplastic organic polymer.
- 20 14. The method of Claim 13 wherein steps (a) and (c) are performed simultaneously.
15. The method of Claim 14 wherein in step (c) said binder material particles are at least partially melted by means of a flame.
16. The method of Claim 15 wherein step (c) is performed using a flame spray
- 25 apparatus.
17. The method of Claim 13 wherein steps (a) and (c) are performed sequentially.
18. The method of Claim 17 wherein in step (c) said binder material particles are at least partially melted by means of a flame.
- 30 19. The method of Claim 16 wherein step (c) is performed using a flame spray apparatus.
20. The method of Claim 17 wherein steps (a) - (d) are conducted at least twice before conducting step (e).

## AMENDED CLAIMS

[received by the International Bureau on 22 March 1993 (22.03.93);  
original claims 14,17-19 cancelled;  
original claims 1-4,6-9,11,12,15,16 and 20 amended;  
other claims unchanged (2 pages)]

1. A method for applying a binder to a mat composed of fibers to form a fiber preform, comprising
  - (a) applying a plurality of particles of an at least partially melted tacky binder material to a mat composed of fibers, the binder material being solid at 25°C, and then
  - (b) cooling said binder material to a temperature at which it is solid such that the particles adhere to the fibers and bind said fibers together to form a fiber preform, the binder material being present in an amount from about 0.25 to about 20 parts per 100 parts by weight mat.
2. The method of Claim 1 wherein said binder material is a thermoplastic organic polymer and said mat is composed of glass, graphite, carbon, or high flexural modulus organic polymer fibers
3. The method of Claim 2 wherein said fibers have a diameter from about 1 to about 1000 microns, and about 1 to about 20 parts by weight binder material are used per 100 parts by weight mat.
4. The method of Claim 3 wherein said binder material is a thermoplastic epoxy resin, and the fibers are glass fibers having an average length of about 0.25 to about 10 inches.
5. The method of Claim 3 wherein the mat is composed of woven or looped glass fibers.
6. A method of preparing a fiber preform, comprising
  - (a) spraying a plurality of particles of a binder material which is solid at 25°C through an energy source such that the particles are at least partially melted so as to become tacky;
  - (b) contacting said particles and a mat composed of fibers; and
  - (c) cooling said particles to a temperature at which they are solid such that the particles adhere to the fibers and bind the fibers together to form a fiber preform, such that the particles are present in an amount of from about 0.25 to about 20 parts per 100 parts by weight mat.
7. The method of Claim 6 wherein said binder material is a thermoplastic organic polymer and said mat is composed of glass, graphite, carbon, or high flexural modulus organic polymer fibers
8. The method of Claim 7 wherein said fibers have a diameter from about 1 to about 1000 microns, and about 1 to about 20 parts by weight binder material are used per 100 parts by weight mat
9. The method of Claim 8 wherein said binder material is a thermoplastic

epoxy resin, and the fibers are glass fibers having an average length of about 0.25 to about 10 inches

10. The method of Claim 8 wherein the mat is composed of woven or looped glass fibers.

5 11. A method for making a fiber preform, comprising the steps of  
(a) applying a plurality of short reinforcing fibers onto a screen to form a shaped mat;  
(b) maintaining said fibers in position on the screen during steps (c) and (d);  
(c) concurrently with or subsequently to step (a), spraying a plurality of particles  
10 of an at least partially melted tacky binder material onto said fibers, said binder material being solid at 25°C; and  
(d) cooling said binder material to a temperature at which it is solid, whereby the binder material adheres to the fibers and binds the fibers together to make a  
fiber preform, the binder material being present in an amount from about 0.25 to  
15 about 20 parts per 100 parts by weight mat, and then  
(e) removing the preform from the screen.

12. The method of Claim 11 wherein said fibers have a diameter from about 1 to about 1000 microns and an average length of about 0.25 to about 4 inches, and about 1 to about 20 parts by weight binder material are used per 100 parts by weight mat.

20 13. The method of Claim 12 wherein said fibers are glass, graphite, carbon or a high flexural modulus organic polymer, and said binder material is a thermoplastic organic polymer.

14. The method of Claim 11 wherein in step (c) said binder material particles are at least partially melted by means of a flame

25 15. The method of Claim 15 wherein the particles are sprayed and partially melted by means of a flame spray apparatus.

16. The method of Claim 11 wherein steps (a) - (d) are conducted at least twice before conducting step (e).

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## INTERNATIONAL SEARCH REPORT

PCT/US 92/08947

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D04H1/60; C08J5/04		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	D04H ; C08J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 7937685B[20] & JP,A,54 043 262 (NIPPON STEEL CHEM. KK.) 5 April 1979 see abstract ---	1,2,6,7
Y	US,A,4 869 950 (ELSEN J.M. ET AL) 26 September 1989 see claim 1 ---	1,2,6,7
X	DATABASE WPIL Derwent Publications Ltd., London, GB; AN 86229623[35] & JP,A,61 160 464 (ASAHI FIBER GLASS KK.) 21 July 1986 see abstract --- -/--	1,2,6,7
<div style="display: flex; justify-content: space-between;"> <div> <p><sup>10</sup> Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
15 JANUARY 1993		21. 01. 93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		NIAOUNAKIS M.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	DATABASE WPIL Derwent Publications Ltd., London, GB; AN 89104908[14] & JP,A,1 052 806 (KANAI H.) 28 February 1989 see abstract ---	1,2,6,7
A	DATABASE WPIL Derwent Publications Ltd., London, GB; AN 85149869[25] & JP,A,60 082 344 (KURARAY KK.) 10 May 1985 see abstract -----	1,2,6,7

## INTERNATIONAL SEARCH REPORT

Int'l application No.

PCT/US 92/08947

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
Not well understandable claims due to clerical errors. Obscure matter:  
(claim 16 → step c), (claim 18 → step c) and (claim 20 → step e)  
One claim mentioned twice: (claims 16 and 19)..  
Claims not searched : 16,18 - 20
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.☐ No protest accompanied the payment of additional search fees.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9208947  
SA 66055

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 15/01/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4869950	26-09-89	None	

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82